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Correlation between stoichiometry and surface structure of the polar $\text{MgAl}_2\text{O}_4(100)$ surface as a function of annealing temperature†

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The correlation between surface structure, stoichiometry and atomic occupancy of the polar $\text{MgAl}_2\text{O}_4(100)$ surface has been studied with an interplay of noncontact atomic force microscopy, X-ray photoelectron spectroscopy and surface X-ray diffraction under ultrahigh vacuum conditions. The Al/Mg ratio is found to significantly increase as the surface is sputtered and annealed in oxygen at intermediate temperatures ranging from 1073–1273 K. The Al excess is explained by the observed surface structure, where the formation of nanometer-sized pits and elongated patches with Al terminated step edges contribute to stabilizing the structure by compensating surface polarity. Surface X-ray diffraction reveals a reduced occupancy in the top two surface layers for both Mg, Al, and O and, moreover, vacancies are preferably located in octahedral sites, indicating that Al and Mg ions interchange sites. The excess of Al and high concentration of octahedral vacancies, very interestingly, indicates that the top few surface layers of the $\text{MgAl}_2\text{O}_4(100)$ adopts a surface structure similar to that of a spinel-like transition Al_2O_3 film. However, after annealing at a high temperature of 1473 K, the Al/Mg ratio restores to its initial value, the occupancy of all elements increases, and the surface transforms into a well-defined structure with large flat terraces and straight step edges, indicating a restoration of the surface stoichiometry. It is proposed that the tetrahedral vacancies at these high temperatures are filled by Mg from the bulk, due to the increased mobility at high annealing temperatures.

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1 Introduction

Metal oxides with the spinel crystal structure adopted from the mineral MgAl_2O_4 (spinel) are a major component of the Earth's upper mantle,¹ and they have great technological importance with fascinating electrical, magnetic, and other physical characteristics. Metal oxide spinels are widely used in the industry in the field of electronics and as refractory materials because of their low cost, high melting points and cubic structure, which explains their uniform thermal expansion.² In geological environments, the structural and chemical variations in spinel oxides are dependent on both pressure–temperature history

and paragenesis, and therefore they can be used as petrogenetic indicators as well.^{3–5} In the field of heterogeneous catalysis, MgAl_2O_4 has a significant applied importance as refractory support materials for *e.g.* Ni, Ru, or Pt catalysts for high temperature reactions, since, compared to pure alumina supports, MgAl_2O_4 generally is more resistant towards solid state reactions at elevated temperatures, which leads to loss of the active catalyst.^{6–8} Moreover, MgAl_2O_4 is utilized as a substrate to epitaxially grow thin spinel films of *e.g.* Mn_3O_4 ,^{9,10} Co_3O_4 ,^{11,12} and also spinel-like transition alumina films.^{13,14}

The chemical versatility of the spinel compounds is enormous, since Mg^{2+} can be exchanged with a wide range of divalent cations, and Al^{3+} can be exchanged with almost any trivalent cation. The cation distribution ranges from the normal distribution with the divalent cation in tetrahedral sites to the inverse distribution, where they occupy the octahedral sites.¹⁵ Furthermore, the anions (O^{2-}) can be replaced by S^{2-} , Se^{2-} or Te^{2-} and when structures like $\gamma\text{-Al}_2\text{O}_3$ and LiFe_5O_8 , which crystallize in a spinel-like structure, are taken into account, one gets a sense of just how versatile the spinel system is.

Here we present a method to obtain highly inert, refractory and atomically flat $\text{MgAl}_2\text{O}_4(100)$ surfaces, which are highly

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useful substrates for growth of films or nanostructures. Furthermore, we characterize the $\text{MgAl}_2\text{O}_4(100)$ surface at a significant number of stages during the preparation process. However, characterizing the atomic-scale surface structure of insulating metal oxides, such as MgAl_2O_4 , is challenging, mainly due to their insulating nature that makes it difficult to use traditional surface science techniques based on electrons or ions. In this study, a combination of three surface sensitive techniques has been used to determine the surface structure of the $\text{MgAl}_2\text{O}_4(100)$ surface as well as the stoichiometry and distribution of cations in the surface layers for different preparation conditions. Noncontact atomic force microscopy (NC-AFM), which is one of the most commonly used techniques for studying insulators with atomic or nanoscale resolution,^{16–18} has been utilized in this study to determine the topological surface structure of $\text{MgAl}_2\text{O}_4(100)$ after annealing to various temperatures. To determine the structural occupancies in the surface layers, surface X-ray diffraction (SXRD) has been used. Unlike NC-AFM and SXRD, X-ray photoelectron spectroscopy (XPS) is limited by the insulating nature of MgAl_2O_4 , and uneven charging of the surface may lead to broadened and shifted peaks. However, a uniform sample charging allowed us to calibrate the XPS spectra and utilize them for quantification of relative occupancies on the $\text{MgAl}_2\text{O}_4(100)$ surface in this study.

2 The $\text{MgAl}_2\text{O}_4(100)$ surface

Magnesium aluminate (MgAl_2O_4) is a metal oxide with the normal spinel structure defining a larger group of spinel minerals, which adopt the formula $(\text{A}_{1-x}\text{B}_x)^{\text{tet}}[\text{A}_x\text{B}_{2-x}]^{\text{oct}}\text{O}_4$, where the parentheses refer to the tetrahedral site, square brackets to the octahedral sites, and x to the inversion parameter.¹⁹ The normal spinel structure ($x = 0$) is characterized by a slightly deformed cubic close packed lattice of oxygen atoms with Mg^{2+} occupying 1/8 of the tetrahedral positions and Al^{3+} occupying 1/2 of the octahedral positions with a unit cell length of 8.086 Å as illustrated in Fig. 1a.²⁰ The oxygen atoms are positioned in double rows, which direction alternate through the layers of the crystal repeating itself in an *abab* manner as illustrated in the surface model in Fig. 1b. The stacking sequence in the [100] direction is $\text{Mg}_2\text{-O}_4\text{-Al}_4\text{-O}_4$, as illustrated in Fig. 1a, which gives rise to two bulk surface terminations, which both are polar. Polarity can be canceled by removal of a certain percentage of the atoms in the surface layer. The surface vacancies will then most likely re-organize and lead to a surface reconstruction in order to fulfill the polar stabilization criteria.²¹ This has for example been observed on the (1×1) -terminated Zn(0001) surface of wurtzite ZnO, where islands and holes with O-terminated edges are created in order to decrease the overall surface Zn concentration.²²

A hypothetical truncation of the MgAl_2O_4 crystal just above the Mg layer creates a fully Mg-terminated, polar surface, and cleaving below the Mg layer creates a polar Al–O-terminated surface with excess O. However, a non-polar stoichiometric surface termination may exist if the Mg-layer is instead split

Fig. 1 (a) Perspective ball model of the MgAl_2O_4 structure showing the stacking in the [100] direction. O ions form a face-centered cubic lattice with Mg ions in tetrahedral sites and Al ions in octahedral sites. (b) Top-view ball model of the $\text{MgAl}_2\text{O}_4(100)$ surface showing a step, the preferred growth direction along the Al and O rows, as well as the square 5.7 Å × 5.7 Å surface unit cell.

between two surfaces leading to a 50% occupancy of Mg and the creation of a (2×2) surface unit cell. Similarly, the Al-layer can be split between two layers leading to a non-polar surface, but these surfaces in general have high surface energies.^{15,23} By theory the Mg-terminated surface with a Mg occupancy of 50% was considered to be the most stable surface termination,^{23,24} however, it was recently experimentally revealed using NC-AFM that the $\text{MgAl}_2\text{O}_4(100)$ surface prepared under UHV conditions in oxygen instead adopts a well-defined unreconstructed Al–O terminated surface with only a modest amount of surface defects.^{25,26} The polarity compensation was instead concluded to be controlled by adsorbed OH-groups on the surface and the so-called antisite defects, where octahedral Al ions interchange with tetrahedral Mg ions in the surface layers. The previous findings were concluded on the basis of the surface structure obtained by extensive annealing in oxygen (10^{-7} mbar), but here we reveal that the surface structures obtained at lower

temperature is sensitive to the exact preparation conditions, and that the resulting surface structure may be explained by different stabilization mechanisms which predominate for different temperatures.

3 Methods

3.1 Sample preparation

The MgAl_2O_4 crystals with EPI polished (100) facets were provided by MTI Corporation. To prepare the crystals for the experiments, they were first sonicated for 30 min in a 1:1 mixture of nitric acid (65%) and water followed by annealing in a tube furnace in air for 5 hours at 1373 K. The samples were then transferred to a standard ultrahigh vacuum (UHV) system with a base pressure lower than 1×10^{-10} mbar. The preparation procedure consisted of sequential sputtering (10 min at 1000 eV Ar ion energy) and annealing (10 min at temperatures ranging from 1073 K to 1473 K). Annealing occurred in 10^{-7} mbar O_2 , unless otherwise stated, utilizing a 2 K s^{-1} temperature up and down ramp. NC-AFM images reveal that surface cleaning in oxygen revealed significantly cleaner surfaces compared to surface cleaning in UHV. However, surface cleaning of the $\text{MgAl}_2\text{O}_4(100)$ surface is rather insensitive to the O_2 pressure, and surface cleaning in range from 10^{-7} mbar to 10^{-6} mbar results in the same surface structure. The temperature was continuously monitored using a Metis MY81 pyrometer supplied by Sensortherm GmbH. Oxygen dosing was started at 373 K while ramping up the temperature and stopped again at 773 K during the subsequent cooling cycle.

3.2 Noncontact atomic force microscopy

NC-AFM images were recorded using a VT-AFM/STM manufactured by Omicron contained within the above-mentioned UHV system. A Nanonis scanning probe microscopy control system was used for the measurements, as well as commercial silicon cantilevers from nanosensors of the SSS-NCH type with nominal tip radii of about 2 nm, resonance frequencies of approximately 330 kHz and force constants of 42 N m^{-1} . Before imaging, the tips were sputtered with Ar^+ ions for 10 s at 800 eV acceleration energy, which has proven to remove the native SiO_2 layer without significantly blunting the tips.²⁷ All NC-AFM images presented in this paper were recorded using the microscope operating in the frequency modulation mode, where the cantilever is excited at its first mechanical resonance frequency to a constant amplitude in close proximity of the surface. The forces between the tip and the surface cause a shift in resonance frequency with respect to the free resonance frequency, this shift is referred to as the frequency shift or simply df . When the tip is raster scanned across the surface, a feedback loop maintains a preset df and the changes in tip position are recorded, thereby creating a topographic image of the surface.

In NC-AFM a contact potential difference (CPD) between the tip and sample generally arises because of the difference in work functions and is given by $U_{\text{CPD}} = (\phi_{\text{tip}} - \phi_{\text{sample}})/e$.¹⁷ In our experiments the CPD was compensated for by applying a

voltage, U_{bias} , on the surface with respect to the tip, and U_{bias} , was monitored and adjusted regularly during recording of images to minimize the electrostatic forces between the tip and sample. All NC-AFM images were analyzed using the Scanning Probe Image Processor (SPIP) from Image Metrology.

3.3 X-ray photoelectron spectroscopy

Surface elemental relative occupancy was monitored using XPS, connected to the same UHV system as mentioned above, using Al $\text{K}\alpha$ radiation with an energy of 1486.6 eV from a source operated at 250 W (SPECS XR 50 source). XPS was recorded from a circular acceptance area of $\varnothing 0.7 \text{ mm}$ at the center part the crystal as set by the analyzer focusing ($\varnothing 7 \text{ mm}$ slit with high magnification, $M = 10$). A SPECS Phoibos 100 analyzer was used to record the XP spectra in normal emission. Survey scans were conducted at binding energies from 0 to 1340 eV, and the O 1s, Al 2s/2p and Mg 2s/2p peaks were analyzed with high resolution using a pass energy of 30 eV. The binding energies of all peaks were referenced to the O 1s peak position of 531.6 eV to account for sample charging,²⁸ which was typically in the range from 5 to 6 eV. The surface charging was found to be constant for all binding energies; therefore all peaks could be calibrated to the O 1s peak, which was the most intense peak in the spectrum. The uniform and constant surface charging is expected to be due to very uniform samples and a spot size larger than the sample size. Thus, for this system, the small spot size used with synchrotron radiation would not be beneficial. Data analysis was performed using CasaXPS (Casa Software Ltd, UK), and the peak areas were determined by integration employing a Shirley-type background. The relative occupancies were determined from the relative peak areas obtained from area integration and correction with the corresponding sensitivity factor calculated from the photoemission cross-section and inelastic mean-free path. For the estimation of the relative occupancies, the areas of the O 1s, Al 2p and Mg 2p peaks were used, and the probing depths taken specifically into account from the corresponding mean free paths (calculated for Al $\text{K}\alpha$) in MgAl_2O_4 are 24.3 Å, 32.8 Å and 33.3 Å, respectively.²⁹ This yields the average relative occupancy of Al, Mg and O in the topmost 3–4 unit cells of the $\text{MgAl}_2\text{O}_4(100)$ representative for the entire sample surface, but it does not reveal information on inhomogeneous distribution within these layers. The occupancy data were checked for systematic errors by utilizing the built-in functionality of CasaXPS, where the uncertainty quantities are calculated using a Monte Carlo procedure assuming the counts per bin obey Poisson behaviour. The XPS spectra were checked using Mg $\text{K}\alpha$ radiation and the conclusions from the data are qualitatively and quantitatively the same.

3.4 Surface X-ray diffraction

The SXRD experiments were performed at the MPI-MF beamline at the Angstrom Quelle Karlsruhe (ANKA) using a photon energy of 10 keV.³⁰ The $\text{MgAl}_2\text{O}_4(100)$ sample was mounted on a portable UHV X-ray diffraction chamber equipped with a separate sputter gun and electron bombardment heating. The sample surface was

prepared by sequential cycles of sputtering (10 min sputtering at 1 keV Ar ion energy) and annealing (20 min at 1423 K in 10^{-6} mbar O_2) and the X-ray data were collected at room temperature if not otherwise stated. Initially, the sample was studied after mild annealing at 623 K in 10^{-6} mbar O_2 for 1 hour without sputtering.

Integrated intensities were obtained from rocking scans with the rotation axis normal to the surface after background subtraction and application of standard correction factors.³¹ Systematic error bars were determined from the comparison of symmetry equivalent rods. For the fit of the 257 symmetry inequivalent structure factors the program package ROD was used.³¹ The data are presented using the (100) surface reciprocal lattice of $MgAl_2O_4$ with $a^* = b^* = 2\pi \times \sqrt{2}/a_{\text{bulk}}$, $c^* = 2\pi/a_{\text{bulk}}$, and $\alpha = \beta = \gamma = 90^\circ$. The bulk lattice constant was refined to $a_{\text{bulk}} = 8.086 \text{ \AA}$.²⁰ For the fitting procedure χ^2 minimization was performed

$$\chi^2 = \frac{1}{(N - P)} \sum_N \frac{|F_{\text{ex},N} - F_{\text{cal},N}|}{\Delta F_{\text{ex},N}},$$

where N is the number of data points, P is the number of fitting parameters, F_{ex} is the experimental structure factor (with error bar ΔF_{ex}) and F_{cal} is the calculated structure factor. The fit is very sensitive to the individual occupancies of the Al, Mg and O sublattices because of their differing structure factors.

4 Results

4.1 NC-AFM: surface structure dependency on annealing temperature

After introduction of the $MgAl_2O_4(100)$ sample to the UHV chamber it was degassed for 3 hours at 773 K in UHV. At this stage, NC-AFM images reveal a flat surface indicated by steps with a typical step height of 2 Å, corresponding to the distance between Al–O layers in the [100] direction (see Fig. 1a). The steps have irregular step edges and the terraces measure up to 300 nm in width. Also, due to the lack of sputtering, the surface still contains a rather high amount of apparent contaminants clearly visible in Fig. 2a. After the sample has been sputtered a few times and mildly annealed in oxygen, NC-AFM images reveal that the contaminants are removed from the surface, the step edges remain irregular, and the terraces grow in size with the largest ones measuring several hundreds of nm (see Fig. 2b). After annealing in oxygen to 1173 K a kind of micro-faceting appears, making the surface rougher on the microscopic scale, which causes the step edges on the macroscopic scale to stand out less clearly as illustrated in Fig. 2c. It is speculated that the polar, O-rich $MgAl_2O_4(100)$ surface is stabilized by nanometer-sized pits with Al terminated edges. Fig. 2d illustrates an example of how such pits can be created by the removal of 42 O, 12 Al and 9 Mg, thus overall removing O from the surface. Every pit created with this size results in a decrease of 30 charge units, and if only the charge contribution from the top Al–O layer is considered, a 59% pit coverage is needed in order to get a completely nonpolar surface. An analysis of several NC-AFM images recorded after a few surface

Low temperature regime

Fig. 2 NC-AFM images recorded in the low temperature regime on the $MgAl_2O_4(100)$ surface after (a) degassing in UHV and (b, c) mild sputtering and annealing in oxygen at temperatures up to 1173 K. The contaminants initially present (a) are desorbed after annealing in oxygen at 1073 K (b), and NC-AFM images recorded after annealing at 1173 K reveal a microfaceted surface (c) and it is speculated that the surface is stabilized by the formation of nanometer-sized pits. (d) Ball model illustrating how rectangular holes with Al terminated edges can be created in the surface.

cleaning cycles in oxygen at 1173 K reveals a pit coverage of $54 \pm 6\%$, which agrees well with the pit coverage needed to obtain a nonpolar surface. All NC-AFM images recorded after annealing up to 1173 K reveal flat surfaces with similar surface structures, and this temperature range is named the low temperature regime.

After additional surface cleaning cycles in oxygen of the $MgAl_2O_4(100)$ surface to temperatures in the intermediate temperature range from 1173 K to 1323 K, NC-AFM images reveal that the micro faceting continues to evolve on the surface as illustrated in Fig. 3a–c. After several sputtering and annealing cycles in oxygen to 1173 K, the nanometer-sized pits become more clearly defined, and upon further increasing the temperature, they transform into elongated patches with a step height of a single Al–O layer (2 Å). A speculative illustration of how these elongated patches can be created on the $MgAl_2O_4(100)$ surface is provided in Fig. 3d, and it is again speculated that the patches have Al terminated step edges. This means that overall O will be removed from the surface, and thereby contributing to stabilize the surface. The patches have a typical length of approximately 60 nm and follow the preferential growth directions along the Al and O rows as illustrated by the white dashed lines in Fig. 3d. After a single annealing cycle in oxygen to 1323 K the patches grow longer to a typical length of a few hundred nm. Furthermore, the stripes begin to coalesce and thereby forming macroscopically large terraces with clearly defined step edges. The step edges are much straighter, than after annealing at lower temperatures, which is

Fig. 3 NC-AFM images recorded in the intermediate temperature regime on the $\text{MgAl}_2\text{O}_4(100)$ surface after (a–c) intermediate sputtering and annealing in oxygen at temperatures ranging from 1173 K to 1323 K. It is speculated that the surface is stabilized by elongated patches in this intermediate temperature regime. (d) Ball model illustrating how nanometer wide elongated patches with Al terminated edges can be created in the surface. Preferential growth directions along the Al and O rows on the $\text{MgAl}_2\text{O}_4(100)$ surface are marked with white dashed lines.

likely due to the higher atom mobility at these intermediate annealing temperatures.

The $\text{MgAl}_2\text{O}_4(100)$ surface changes radically after several sputtering and annealing cycles in oxygen to high temperatures ranging from 1373 K to 1473 K, where the elongated patches coalesce to form a perfect crystalline surface, as illustrated in Fig. 4. After a single sputtering and annealing cycle in oxygen in this regime, the terrace widths are typically between 50 and 100 nm, the typical step height is a single Al–O layer (2 Å), and the amount of kinks on the step edges decreases to a minimum. After further sputtering and annealing, the step edge kinks outgrow completely and the size of the terraces continues to increase up to a width of approximately 400 nm, as illustrated in Fig. 4c and d. At this stage the $\text{MgAl}_2\text{O}_4(100)$ surface is atomically flat and the surface structure is unchanged even after several sputtering and annealing cycles in oxygen to 1473 K. It is intriguing that a flat unreconstructed surface can be prepared for this polar facet and the atomic-scale structure of this surface has previously been discussed,²⁵ where the two proposed surface stabilization mechanisms are, firstly, the presence of OH groups and, secondly, stable so-called Mg–Al antisites, which become a thermodynamically stable and integral part of the surface. It is speculated that H diffusion from the bulk sets in at high temperatures, however still below 1023 K, where H has been observed to desorb from the surface by temperature programmed desorption, which is in agreement with DFT surface energy calculations on the

Fig. 4 NC-AFM images recorded in the high temperature regime on the $\text{MgAl}_2\text{O}_4(100)$ surface after sputtering and annealing in oxygen at temperatures of (a, b) 1373 K and (c, d) 1473 K. The patches observed at lower temperatures coalesce to form after annealing to 1373 K (a). Upon further sputtering and annealing to 1473 K, the terrace widths increase while the surface become atomically flat (b, c). The high stability of the surface is reflected by its unchanged surface structure even after several sputtering and annealing cycles (d).

$\text{MgAl}_2\text{O}_4(100)$ surface previously published.²⁵ Following an annealing cycle as the sample cools down below 1023 K, it is likely that H present on the surface enables the formation of surface OH groups.

4.2 X-ray photoelectron spectroscopy

To follow changes in the surface composition due to sputtering and annealing in oxygen of the $\text{MgAl}_2\text{O}_4(100)$ surface, XPS survey scans as well as high resolution scans of the O 1s region and the Al/Mg 2s/2p regions were recorded. The survey scans reveal clean $\text{MgAl}_2\text{O}_4(100)$ surfaces, with peaks belonging to either Mg, Al or O. As expected, C was detected as an impurity, however, only prior to sputtering and annealing of the surface. Fig. 5 shows typical spectra of the O 1s and Al/Mg 2s/2p regions. Due to the insulating nature of the sample a significant amount of charging towards higher binding energies is observed, and in Fig. 5, all charged and uncharged peaks are labeled, as are the Auger peaks and ghost peaks, which arise because the X-ray source is not completely monochromatic.

To monitor changes in the surface composition from the XPS data, we define the relative occupancies as the relative peak areas of O 1s, Al 2p and Mg 2p after correction with the corresponding sensitivity factors (the sum of the relative occupancies equals 100%). The relative occupancies of the surface layers as well as the Al/Mg ratio, as illustrated in Fig. 6, are highly dependent on the number of sputtering and annealing cycles, where especially the annealing temperature plays an

Fig. 5 High resolution XPS region scans of the (a) O 1s region and the (b) Al/Mg 2s/2p regions recorded on the $\text{MgAl}_2\text{O}_4(100)$ surface after several sputtering and annealing cycles in the high temperature regime. Due to the insulating nature of the surface, the most significant peaks are the charged Al 2s/2p and Mg 2s/2p peaks. Furthermore, the Al KLL Auger peak, and ghost peaks belonging to (a) O 1s and (b) Al 2p are observed.

important role. The XPS data reveal an O relative occupancy, which is in general around 10% lower relative to its nominal stoichiometric value of 57% (4/7), while the total cation relative occupancy consequently is higher than its stoichiometric value of 43% (3/7). Considering the Al/Mg ratio, it increases steadily from 2.0:1, prior to sputtering and after mild annealing in UHV in the low temperature regime, to 3.4:1 after sputtering and annealing in the intermediate temperature regime, *i.e.* corresponding to an Al excess. As NC-AFM images reveal the formation of nanometer-sized pits and at a later stage elongated patches after the surface has been annealed at intermediate temperatures, it supports the model in which the pits and elongated patches contain Al-terminated step edges, as illustrated in Fig. 2d and 3d, which result in an overall removal of O and Mg from the surface,

Fig. 6 (a) Relative occupancies as calculated from XPS recorded on the $\text{MgAl}_2\text{O}_4(100)$ surface and (b) Al/Mg ratio as a function of sputtering and annealing cycles at increasing temperatures. The probing depths were 33.3 Å, 32.8 Å and 24.3 Å for Mg, Al, and O, respectively.

which explains the increase in the Al/Mg ratio. Interestingly, after annealing in the high temperature regime, the Al/Mg ratio decreases to 2.1:1, *i.e.* close to the initial value of 2.0:1. At this stage, the surface corresponds to a rather flat, perfectly crystalline surface, as imaged by NC-AFM, where pits or elongated patches are no longer observed, which again supports that the surfaces at lower temperatures are Al enriched by the formation of microfacets and pits. Clearly a faceted surface can accommodate more Al than the flatter surfaces. In this regard, we speculate that a driving force for the formation of the flatter, stoichiometric MgAl_2O_4 surface could be due to the onset of desorption of undercoordinated Al (or AlO_x) species at the highest temperatures. In addition, the hypothesis regarding H diffusing from the bulk to the $\text{MgAl}_2\text{O}_4(100)$ surface to form hydroxyl groups could in principle be observed in the hydroxyl shoulder at a higher binding energy of the O 1s peak,⁹ but unfortunately a definite assignment of OH in the peak in our XPS data was not possible due to 2 eV broadening from inhomogeneous charging of the surface.

4.3 Surface X-ray diffraction

Surface X-ray diffraction data have been recorded for $\text{MgAl}_2\text{O}_4(100)$ samples representative of the three types of surface structures in Fig. 2–4, respectively, since this provided complementary

information regarding the exact surface structure, possible surface reconstruction and by means of fitting to the structure factors it is possible to extract information about the oxygen and cation occupancies in the tetrahedral and octahedral sites of spinel, respectively.

Experimental structure factors from the $\text{MgAl}_2\text{O}_4(100)$ surface have been measured from the following crystal truncation rods: (1,0), (2,0), (1,1), (2,2), (3,0), (1,2) and (3,1). The structure factors and best fits to the experimental data are plotted in Fig. 7a. It gets evident that the X-ray structure factors undergo significant changes for the different preparation conditions, which reflect the change in the near surface sublattice occupation profiles, as discussed in the following. The initial fit was performed using bulk terminated surfaces with the Al and O-Al termination, yielding the lowest χ^2 value for an O-Al terminated surface (goodness of fit parameter $\chi^2 = 10$ as compared to $\chi^2 = 16$). The structure factor of the bulk-terminated Mg terminated surface is identical to the structure factor of the Al-O terminated surface because of symmetry reasons. The Mg terminated surface is however expected to exist in a 2×2 reconstructed state but the absence of fractional order spots when scanning the (h,k) space for fixed l values rules out reconstructions of the $\text{MgAl}_2\text{O}_4(100)$

surface, such as the 2×2 reconstruction of the 50% Mg terminated surface. The Mg terminated surface can furthermore be ruled out based on its high surface energy.²⁵ Since the experimental X-ray structure factors exhibited a fourfold symmetry (as compared to the expected lower two fold symmetry of the (100) surface), two symmetry inequivalent terraces were included in the fit (as in Fig. 1b, corresponding to a step height of 2.02 Å, in agreement with the step height observed by AFM).

During the further refinement of the O-Al terminated surface, atomic displacements were allowed in accordance with the broken symmetry induced by the presence of the surface. In addition, the occupation probability of the oxygen atoms in the two topmost layers were allowed to vary, as well as the occupation of Al and Mg sites to deeper layers, taking vacancies into account. Please note that the reciprocal lattice of a half-infinite crystal is intrinsically surface sensitive. In the minimum of the CTRs only scattering of the topmost layer contributes because of the destructive interference for the amplitude of all lower lying unit cells. Approaching the Bragg reflections at integer L values, more and more bulk layers contribute to the signal.³² We find that the overall atomic displacements from their bulk positions are small (< 0.25 Å). Most prominently, for the low T

Fig. 7 (a) Crystal truncation rod data obtained at different stages of preparation. Red circles, low temperature regime; black squares, intermediate temperature regime; blue triangles, high temperature regime; black dots, bulk terminated surface. (b) Individual O, Al and Mg sublattice layer resolved atomic occupancies of the $\text{MgAl}_2\text{O}_4(100)$ surface after sputtering and annealing to different temperature regimes as determined by SXRD.

and intermediate T data we find that the distance of the oxygen rows on the surface and in the first subsurface layer is contracted, in agreement with recent results.²⁵ For the low T data, the first layer oxygen row distance is found to be expanded, which may be explained by the high number of O_h Al vacancies in the topmost layer (see below). A good fit on most of the crystal truncation rods can be obtained by the inclusion of occupancies and displacements of the two topmost layers (the full sets of atomic positions are given in the ESI†); the (2,0) rod, however, turns out to be very sensitive to the occupancy profile of the Al and Mg sublattices. The fit of the (2,0) rod can therefore be improved by the inclusion of Mg and Al vacancies in the few-percent regime down to 13 Å into the bulk.

In Fig. 7b the fitted occupancies of the Mg (tetrahedral sites, green), Al (octahedral sites, grey) and O (red) sites as compared with the ideal spinel structure have been plotted for the surfaces representative of the three structure types, as previously mentioned, for the first 5 layers counted from the surface. It is important to point out that X-ray diffraction is dependent on the atomic number (Z), but since Mg ($Z = 8$) and Al ($Z = 9$) have almost the same Z , it is the occupancy and not the element type which is probed in the experiment. Overall, the occupancy profiles are in-line with a smooth surface, which is also confirmed by the root mean square roughness of 1.7 Å obtained from X-ray reflectivity measurements (not shown).

The SXRD data recorded on $MgAl_2O_4(100)$ after the first mild annealing cycle at 10^{-6} mbar oxygen at 623 K, which is representative of surfaces annealed in the low temperature regime, reveal a reduced site occupancy of both O, Mg, and Al sites. The reduced occupancies are observed in the first four layers, whereas it is restored to the bulk value in the fifth layer. A similar reduced occupancy is also observed after additional sputtering, thus representing surfaces annealed in the intermediate temperature range, as illustrated in Fig. 7b, although the bulk value is now restored already in the third layer. Considering that SXRD is an averaging technique, the reduced site occupancy can be rationalized by the observed microstructure from the NC-AFM data. The general reduction in the site occupancy of all atoms may then be explained by the formation of pits which are much smaller than the coherence length in SXRD and the depth of the disturbed concentration profile in Fig. 7b is in full accordance with *e.g.* the pit and island structure seen in the AFM images in Fig. 3.

The detailed distribution among the site occupancy in the different layers shows several interesting observations. In the low temperature situation, the O and tetrahedral sites (Mg) are reduced with the same fraction whereas the Al site is significantly lower than both of these in the first two layers. This is at first hand incompatible with the Al enrichment seen with XPS, but the effect can be rationalized by site exchange in which Al is placed in Mg sites leading to the formation of domains with the inverse spinel structure or defective Al spinels. Moreover, there is a possibility of Al being located in Mg sites at the step edges. After annealing at intermediate temperatures, the trend is reverted and now the occupancy of the O and octahedral sites is similar, while the occupancy of the tetrahedral cation sites in the top layer is severely decreased.

Finally, after several sputtering and annealing cycles, representative of surfaces annealed in the high temperature regime, the occupancies of both octahedral and tetrahedral sites in the top layer increase. In the model where deviation from bulk site occupancies is explained by the monolayer pits, this is fully compatible with the surface flattening observed in the AFM data and the restoration of the initial stoichiometry of the surface at the high temperature regime from the XPS data. Interestingly, the remaining cation vacancies in the top layer are exclusively located on tetrahedral sites, whereas the second layer of the surface still contains a significant amount of vacancies on the octahedral sites.

Discussion

NC-AFM reveals a flat $MgAl_2O_4(100)$ surface after sputtering and annealing in oxygen at low temperatures, a rougher surface after annealing in oxygen at intermediate temperatures, and finally again a flat surface after annealing in oxygen at high temperatures. XPS reveals an increasing Al/Mg ratio with increasing annealing temperature. However, after annealing in the high temperature regime, the Al/Mg ratio restores to a level similar to its initial value. We propose that the $MgAl_2O_4(100)$ surface, in the intermediate temperature regime, is stabilized by the formation of nanometer-sized pits and elongated patches with Al terminated step edges. As the surface regains its flatness by adopting a perfectly crystalline surface structure after annealing in the high temperature regime, the drop in the Al/Mg ratio is explained by the low amount of Al terminated step edges on the surface.

Initially, as the sample is introduced to the UHV system the Al/Mg ratio is determined to be 2.0:1. After one cycle of sputtering and annealing of the surface in the intermediate temperature regime, the Al/Mg ratio significantly increases to 2.6:1 after annealing in oxygen to 1073 K, meaning that Mg is leaving the surface layers. The formation of Al terminated pits and elongated patches is a possible way for the surface to relieve surface polarity.²² Overall O and Mg will be removed from the surface and thereby cancelling the theoretical polarity of an Al–O terminated $MgAl_2O_4(100)$ surface. In addition to the formation of nanometer-sized pits and elongated patches, a contribution from preferential sputtering of Mg is likely to occur. Mg is tetrahedrally coordinated to four O, while Al is octahedrally coordinated to six O, so it is a likely scenario that Mg is preferentially sputtered off the surface, possibly in the form of MgO.

After several sputtering and annealing cycles in oxygen in the intermediate temperature regime, the Al/Mg ratio peaks at a value of 3.4:1, meaning that only 67% of the original Mg content in the surface layers is still present. At this stage, NC-AFM images reveal a heavily faceted surface with elongated patches along the two preferred growth directions. The patches contain a non-stoichiometric repeat unit of 3 Mg, 8 Al, and 12 O ions, with Al atoms in the surface layer and Mg below, thereby contributing to the further increase in Al/Mg ratio.

The occupancies, as determined by SXRD after mild sputtering and annealing in oxygen, reveal that mainly octahedral vacancies are present. So in order to satisfy the Al/Mg ratio as determined by XPS, approximately every second tetrahedral Mg site in the surface layers must be replaced with Al. The excess Al present on the surface, very interestingly, gives the surface layers more character of a transition alumina phase, e.g. γ -, δ -, or η - Al_2O_3 , which can be grown as thicker layers by Al deposition and oxidation on MgAl_2O_4 .¹³ Many of the transition aluminas crystallize in the spinel structure, and to directly compare the spinel-like transition alumina structure to the structure of MgAl_2O_4 , in principle, two thirds of the Mg atoms are replaced with Al, while the last one third of the Mg-sites are vacancies, to satisfy the alumina stoichiometry.

After sputtering and annealing in oxygen at intermediate temperatures, the elongated patches on the surface are more clearly defined, but the equilibrium surface structure at this temperature is not observed before several sputtering and annealing cycles in oxygen have been conducted, which causes the patches to completely vanish in favor of the formation of larger terraces with straighter step edges. This is compatible with the occupancies determined by SXRD, where the cation vacancies are restricted to the topmost surface. Both tetrahedral and octahedral vacancies are present with tetrahedral vacancies being favored. This means that Al ions, at this intermediate preparation stage, return to the octahedral sites, which is their preferred location in the normal spinel structure.

As the surface is sputtered and annealed in oxygen at high temperatures, NC-AFM reveals a flatter surface with straighter step edges and the terrace widths are often several hundreds of nm wide. At this point, the Al/Mg ratio has dropped to 2.1:1, most likely due to two factors. Firstly, the surface is now atomically flat, so the Al terminated elongated patches are no longer present, and secondly, the bulk Mg ions have a much higher mobility at this high annealing temperature, thus indicating that Mg from the bulk crystal has diffused to the surface layers of the $\text{MgAl}_2\text{O}_4(100)$ crystal. However, the XPS data suggest that Mg vacancies are still slightly favored above Al vacancies. The occupancies determined by SXRD show that the total amount of cation vacancies has decreased compared to the intermediate cleaning stages, and octahedral/tetrahedral vacancies are equally favored. However, tetrahedral vacancies are preferred in the top layer, while octahedral vacancies are preferred in the second layer. The structurally well-defined NC-AFM images of the surface after annealing in oxygen at high temperatures agree well with the lower Al/Mg ratio, as determined from XPS, and the occupancies from SXRD, where the occupancies generally increase with the number of sputtering and annealing cycles.

Conclusions

We have studied the correlation between surface structure and stoichiometry of the $\text{MgAl}_2\text{O}_4(100)$ surface at several stages of sputtering and annealing in oxygen at a wide range of

annealing temperatures. NC-AFM images reveal an initially flat $\text{MgAl}_2\text{O}_4(100)$ surface, which becomes rougher after annealing at intermediate temperatures and finally becomes flat again after being annealed in oxygen at high temperatures up to 1473 K. The Al/Mg as determined from XPS is shown to severely increase as a function of the annealing temperature, which can be explained by preferential sputtering of Mg as well as the formation of a rougher surface with nanometer-sized pits and elongated patches, with Al terminated edges. Occupancies determined from SXRD reveal that octahedral vacancies are favored, indicating that Al diffuses into the tetrahedral sites, after approximately half of the Mg originally present in the surface layers has left the surface. At annealing temperatures of 1473 K, a part of the Mg vacancies in the surface layers is proposed to be filled by Mg from the bulk, due to the higher mobility at this high annealing temperature.

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